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(54) Title of the Invention: Radiation Image Conversion Panel

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SPECIFICATION

1. Title of the Invention

Radiation Image Conversion Panel

2. Claims

A radiation image conversion panel comprising a support having a metal surface; a stimulable phosphor layer; and a protective layer for the stimulable phosphor layer,

wherein said radiation image conversion panel is characterized in that a transparent thin film layer is provided over the metal surface of the support, and the stimulable phosphor layer is provided over this transparent thin film layer.

3. Detailed Description of the Invention

Field of Industrial Utilization

The present invention relates to a radiation image conversion panel that features a stimulable phosphor layer, and more particularly relates to a radiation image conversion panel that can provide radiation images with a practically

high level of radiation sensitivity and sharpness.

Prior Art

In the field of medicine, for example, radiation images such as X-ray images are commonly used in the diagnosis of diseases.

So-called radiophotography is a standard method for obtaining X-ray images, in which X-rays transmitted through a subject are directed at a phosphor layer (fluorescent screen) to generate visible light, and this visible light is then directed at a film made from a silver salt, and the film is developed, just as in conventional photography.

In recent years, however, a method has been proposed for extracting images directly from the phosphor layer, without using a film coated with a silver salt. In this method, the radiation transmitted through a subject is absorbed by a phosphor, after which this phosphor is excited with light or thermal energy, for instance, which causes the radiation energy absorbed and accumulated in the phosphor to radiate as fluorescence, and this fluorescence is detected and imaged.

For example, U.S. Patent 3,859,527 and Japanese Laid-Open Patent Application S55-12144 disclose a radiation image conversion method in which a stimulable phosphor is employed and visible light or infrared rays are used as the

stimulating light. This method employs a radiation image conversion panel comprising a stimulable phosphor layer formed over a support. Here, radiation transmitted through a subject is directed at the stimulable phosphor layer to accumulate radiation energy [in a pattern] corresponding to the degree to which the various parts of the subject transmit radiation, thereby forming a latent image. After this, the stimulable phosphor layer is scanned with the stimulating light to cause the radiation energy accumulated in the various areas to radiate, an optical signal based on the intensity of this light is subjected to photo-electric conversion, for example, and this product is imaged with an image reproduction apparatus. The final image is reproduced either as a hard copy or on a CRT.

The radiation image conversion panel having a stimulable layer used in this radiation image conversion method must have high radiation absorption and photo-electric conversion rates (hereinafter these characteristics will be collectively referred to as "radiation sensitivity"), on a par with those of the above-mentioned radiophotography method that makes use of a fluorescent screen, and furthermore the image needs to have good graininess and high sharpness.

It is common knowledge that the sharpness of the image in a conventional radiophotography method is determined by the spread of the instantaneous emission of the phosphor

(emission upon irradiation) in the fluorescent screen, whereas the sharpness of the image in a radiation image conversion method that makes use of a stimulable phosphor is determined not by the spread of the stimulated emission of the stimulable phosphor in the radiation image conversion panel, that is, not by the spread of the emission of the phosphor as in a radiophotography method, but rather by the spread of the stimulating light within the panel. More specifically, in this radiation image conversion method, the radiation image information accumulated in the radiation image conversion panel is extracted in time series, so preferably all of the stimulated emission generated by the stimulating light emitted at a certain time (ti) is collected and recorded as the output from certain pixels (xi , yi) on the panel from which the stimulating light was emitted during that time, but if the stimulating light is spread out in the panel by scattering or the like so that even the stimulable phosphor present on the outside of the irradiated pixels (xi , yi) is stimulated, then the output from a broader area than that of these pixels (xi , yi) will end up being recorded as the output of these pixels. Consequently, if the stimulated emission generated by the stimulating light emitted at a certain time (ti) consists solely of the emission from those pixels (xi , yi) on the panel actually irradiated with the stimulating light at the time (ti), then the emission, regardless of its spread, will have no effect on the sharpness

of the resulting image.

In light of this situation, several methods have been proposed for improving the sharpness of radiation images.

For example, Japanese Laid-Open Patent Application S62-133399 discloses a panel aspect characterized in that the above-mentioned radiation image conversion panel is formed by the successive lamination of a support, a light reflecting layer, and a stimulable phosphor layer, and the reflecting surface of this light reflecting layer is a metal surface (hereinafter referred to as "light reflecting metal layer"). With this art, the stimulating light does not pass into the light reflecting metal layer, so there is no scattering of light linked to the thickness of the light reflecting layer as in the case of a conventional light reflecting white pigment layer, nor is the light transmitted all the way to the support and scattered within the support, so there is no decrease in the sharpness of the read image.

Problems Which the Invention is Intended to Solve

With the art discussed in the above-mentioned Japanese Laid-Open Patent Application S62-133399, however, the metal surface of the support, that is, the light reflecting metal layer, is in direct contact with the phosphor layer, so in the step of forming the phosphor layer, or in the subsequent heat treatment step (annealing), or as time passes after

formation, the phosphor layer and the metal on the surface of the support may undergo chemical reactions that degrade the phosphor layer and lower the radiation sensitivity, or there may be variance in the light transmissivity and reflectance in the metal layer.

In view of this, it is an object of the present invention to provide a radiation image conversion panel whose structure prevents degradation of the phosphor layer and the metal surface of the support, and with which the radiation sensitivity and image sharpness are both good.

Means Used to Solve the Above-Mentioned Problems

The inventors conducted diligent research aimed at achieving the stated object, and as a result arrived at the present invention upon discovering that degradation of the phosphor layer and the metal surface of the support can be prevented by interposing a transparent thin film layer between the phosphor layer and the support having a metal surface.

Specifically, the present invention is a radiation image conversion panel comprising a support having a metal surface, a stimulable phosphor layer, and a protective layer for the stimulable phosphor layer, wherein said radiation image conversion panel is characterized in that a transparent thin film layer is provided over the metal surface of the

support, and the stimulable phosphor layer is provided over this transparent thin film layer.

The present invention will now be described in specific terms.

Fig. 1 illustrates an example of the radiation image conversion panel of the present invention. Reference numeral 1 is a support, 2 is a transparent thin film layer, 3 is a stimulable phosphor layer, and 4 is a protective layer.

The support 1 comprises a non-metal substrate 1A and a metal layer 1B provided on one side of this substrate 1A. This metal layer 1B constitutes the metal surface of the support 1. This metal layer 1B functions as both a light reflecting layer and a light blocking layer. This metal layer 1B may instead have a laminated structure consisting of separate layers, one having the function of a light reflecting layer and one a light blocking layer.

The transparent thin film layer 2 is provided over the metal layer 1B of the support 1, and the stimulable phosphor layer 3 is provided over this transparent thin film layer 2. Specifically, the transparent thin film layer 2 is provided between the stimulable phosphor layer 3 and the metal layer 1B (the metal surface) of the support 1, and prevents contact between the two. The protective layer 4 is provided over the stimulable phosphor layer 3 with a space 4A therebetween. This space 4A is filled with dry nitrogen gas or the like.

Fig. 2 illustrates another example of the radiation image conversion panel of the present invention, in which the transparent thin film layer 2, the stimulable phosphor layer 3, and the protective layer 4 are successively provided over a metal support 1'. Specifically, in this example the metal support 1' itself functions as the metal layer 1B in Fig. 1.

The transparent thin film layer 2 must be a thin film that is transparent in order to prevent light scattering. In specific terms, the transparent thin film layer 2 preferably has an optical transmissivity of at least 50% with respect to light with a wavelength of 350 to 800 nm. Furthermore, if a colored layer is provided to the side closer to where the stimulating light is incident than the metal surface of the support 1 (discussed later), then the optical transmissivity should be at least 80% with respect to light with a wavelength of 350 to 800 nm. The thickness of the transparent thin film layer 2 is preferably 10 to 3 × 105 Å, with 103 to 104 Å being particularly favorable in the case of an inorganic compound, and 104 to 105 Å in the case of an organic compound.

The transparent thin film layer 2 must also be chemically stable so that it will not degrade the stimulable phosphor layer 3 or the metal surface of the support 1 or 1'. Therefore, favorable examples of the material of which the transparent thin film layer 2 is made include oxides,

nitrides, fluorides, carbides, polymers, and gelatin. Specifically, it is preferable to use SiO_2, Al_2O_2, TiO_2, or another such oxide, MgF_2, CaF_2, or another such fluoride, SiC or another such carbide, SiN or another such nitride, PET, vinyl alcohol film, or another such polymer, or gelatin, for example.

There are no particular restrictions on the means for forming the transparent thin film layer 2, and various thin film formation methods can be employed. Specific examples include vacuum metallizing, sputtering, ion plating, and coating.

The metal layer 1B in Fig. 1 functions as both a light reflecting layer and a light blocking layer, and it must be a metal surface with a different optical density, that is, a different reflectance, at the interface with its adjacent layer.

This metal layer 1B may be formed by vacuum metallizing, sputtering, ion plating, or [regular] plating, or may be formed by the lamination of metal foil. In particular, if a vapor phase deposition method such as metallizing is used, it will be easier to form the metal layer 1B, and the metal layer 1B can be formed easily regardless of the roughness of the surface of the non-metal substrate 1A and so forth.

Examples of the metal that makes up the metal layer 1B include aluminum, gold, silver, copper, chromium, nickel, platinum, rhodium, and tin.

The thickness of the metal layer 1B is preferably 0.01 to 50 μm, and the average reflectance with respect to light in the stimulating light wavelength band should be at least 50%, and particularly at least 70%. This average reflectance can be measured with an integrating sphere type of spectrophotometer.

The metal layer 1B preferably has a transmissivity of no more than 1% with respect to light of 350 to 800 nm.

Fig. 1 is an example in which the non-metal substrate 1A is used, and glass, a ceramic, any of various macromolecular materials, or the like can be used as this non-metal material. Specific examples include quartz glass, chemically reinforced glass, and other such glass, ceramics such as sintered sheets of zirconia, alumina, or crystallized glass, and plastic films such as cellulose acetate films, polyester films, polyethylene terephthalate films, polyamide films, polyimide films, triacetate films, and polycarbonate films.

Fig. 2 is an example in which the metal support 1' is used, and aluminum, aluminum-magnesium alloys, iron, stainless steel, copper, chromium, lead, or another such metal sheet can be used as this metal support 1'.

The thickness of the substrate 1A or the support 1' will vary with the materials thereof and other factors, but 100 μm to 5 mm is generally favorable, and a range of 200 μm to 2 mm is particularly good in terms of ease of handling.

The stimulable phosphor layer 3 is preferably formed by vacuum metallizing (hereinafter referred to as "metallizing" for the sake of simplicity), sputtering, CVD, ion plating, or other such vapor phase deposition method, or by a coating method in which a stimulable phosphor or a phosphor paint prepared by suspending or dissolving a dispersant or the like in a binder is applied in a single layer or in multiple layers separated by function.

If the stimulable phosphor layer is formed by metallizing, the support having a metal surface is placed in a metallizing apparatus, after which the inside of the apparatus is evacuated to a degree of vacuum of about 10-6 Torr. Next, at least one type of stimulable phosphor is heated and evaporated by resistance heating, with an electron beam, or by another such method to deposit the stimulable phosphor in the specified thickness on the metal surface of the support.

As a result, the stimulable phosphor layer 3 containing no binder is formed, but it is also possible to form the stimulable phosphor layer in two or more steps in the metallizing step. It is also possible in the metallizing step to perform co-metallizing using a plurality of resistance heaters or electron beams.

Upon completion of the metallizing, a protective layer is provided as needed on the opposite side of the stimulable phosphor layer from the support side, either directly or via

a space, thereby manufacturing the radiation image conversion panel of the present invention. If the stimulable phosphor layer is provided directly over the protective layer, then the sequence may instead be such that the stimulable phosphor layer is formed over the protective layer, after which this product is provided to the support.

In the metallizing, it is also possible to subject the stimulable phosphor raw material to co-metallizing using a plurality of resistance heaters or electron beams, and form the stimulable phosphor layer simultaneously with the synthesis of the desired stimulable phosphor on the metal surface of the support.

Furthermore, in this metallizing method, the component to be metallized (the support or the protective layer) may be cooled or heated as needed during the metallizing. The stimulable phosphor layer may also be subjected to a heat treatment (annealing) upon completion of the metallizing. Reactive metallizing may also be performed as needed, in which a gas such as O_2 or H_2 is introduced.

If the stimulable phosphor layer is formed by sputtering, then just as with metallizing, a support having a metal surface is placed in the sputtering apparatus, the inside of the apparatus is first evacuated to a degree of

vacuum of about 10-6 Torr,[1] and then an inert gas such as Ar or Ne is introduced as a sputtering gas into the sputtering apparatus to bring the pressure up to about 10-2 Torr.

Sputtering is then performed using a stimulable phosphor as the target, and a stimulable phosphor layer is deposited in the specified thickness on the metal surface of the support.

In this sputtering step, just as with metallizing, it is also possible for the stimulable phosphor layer to be formed in two or more steps. Another possibility is for the stimulable phosphor layer to be formed by sputtering a plurality of targets each composed of a different stimulable phosphor, either simultaneously or successively.

Upon completion of this sputtering, just as with metallizing, a protective layer is provided as needed on the opposite side of the stimulable phosphor layer from the support side, either directly or via a space, thereby manufacturing the radiation image conversion panel of the present invention. If the stimulable phosphor layer is provided directly over the protective layer, then the sequence may instead be such that the stimulable phosphor layer is formed over the protective layer, after which this product is provided to the support.

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[1] Translator's note: Many of the superscripts in the original are of poor legibility.

In this sputtering, it is also possible to use a plurality of stimulable phosphor raw materials as targets and sputter these either simultaneously or successively so as to form the stimulable phosphor layer simultaneously with the synthesis of the desired stimulable phosphor on the metal surface of the support. Reactive sputtering, in which a gas such as O_2 or H_2 is introduced, may also be performed as needed in this sputtering method.

Furthermore, in this sputtering method, the component to be metallized (the support or the protective layer) may be cooled or heated as needed during the sputtering. The stimulable phosphor layer may also be subjected to a heat treatment upon completion of the sputtering.

In the step of forming the stimulable phosphor layer 3 by vapor phase deposition, the rate at which the stimulable phosphor layer is deposited is preferably 0.1 to 50 μm/min. Productivity will be low if the deposition rate is too low, but the deposition rate will be difficult to control if it is too high.

Also, in the step of forming the stimulable phosphor layer 3 by vapor phase deposition, the temperature of the support 1 is preferably 400°C or lower. If this temperature is too high, crystallization will proceed and tend to reduce the sharpness of the image.

The effect of the present invention is greater when the panel is produced by a vapor phase deposition method

because the phosphor is in direct contact with the metal.

When the stimulable phosphor layer is formed by coating, the binder can be any one ordinarily used in layer formation, such as gelatin and other proteins, dextran and other polysaccharides, or gum arabic, polyvinyl butyral, polyvinyl acetate, nitrocellulose, ethyl cellulose, a vinylidene chloride/vinyl chloride copolymer, polymethyl methacrylate, a vinyl chloride/vinyl acetate copolymer, polyurethane, cellulose acetate butyrate, or polyvinyl alcohol. The binder is generally used in an amount of 0.01 to 1 weight part per weight part of stimulable phosphor. However, a small binder content is preferable in terms of the sensitivity and sharpness of the resulting radiation image conversion panel, and a range of 0.03 to 0.2 weight part is preferred from the standpoint of striking a good balance with ease of coating.

A stimulable phosphor paint can be prepared by using a ball mill, sand mill, attriter, triple roll mill, high-speed impeller disperser, Kady mill, ultrasonic disperser, or the like. The paint thus prepared is applied over the support using a doctor blade, roll coater, knife coater, or the like, and the coating is dried to form the stimulable phosphor layer. The stimulable phosphor layer and the support may also be bonded together after the protective layer has been coated with the above-mentioned paint and dried.

Stearic acid, phthalic acid, caproic acid, a lipophilic surfactant, or another such dispersant may also be mixed into the stimulable phosphor layer paint in an effort to improve the dispersibility of the phosphor particles in the stimulable phosphor layer. A plasticizer for the binder may also be added as needed.

Examples of the above-mentioned plasticizer include phthalic esters such as diethyl phthalate and dibutyl phthalate; phosphoric esters such as tricresyl phosphate and triphenyl phosphate; aliphatic dibasic acid esters such as diisodecyl succinate and dioctyl adipate; and glycolic esters such as ethylphthalyethyl glycolate and butylphthalylbutyl glycolate.

Examples of solvents used for preparing the paint in which the stimulable phosphor is suspended include lower alcohols such as methanol, ethanol, isopropanol, and n-butanol; ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; ester dioxanes of a lower fatty acid and lower alcohol such as methyl acetate, ethyl acetate, and n-butyl acetate; ethers such as ethylene glycol monoethyl ether, and ethylene glycol monomethyl ether; aromatics such as triol and xylol; halogenated hydrocarbons such as methylene chloride and ethylene chloride; and mixtures of these.

Whether vapor phase deposition or coating is employed, the thickness of the stimulable phosphor layer 3 will vary

with the targeted radiation sensitivity of the radiation image conversion panel, the type of stimulable phosphor, and other such factors, but 30 to 1000 μm is favorable, and 50 to 500 μm is particularly good. If the stimulable phosphor layer 3 is too thin, there will be a decrease in radiation absorption, so radiation sensitivity will suffer.

The protective layer 4 is provided in order to chemically or physically protect the stimulable phosphor layer 3. This protective layer 4 may be provided via the space 4A as shown in Figs. 1 or 2, or it may be formed by directly coating the stimulable phosphor layer with a coating solution for the protective layer. A separately formed protective layer may also be bonded over the stimulable phosphor layer.

When the protective layer 4 is provided via the space 4A, the material that makes up the protective layer is one that has good transparency and can be formed into a sheet. In order for it to efficiently transmit the stimulating light and stimulated emission, the protective layer preferably exhibits high transmissivity over a wide range of wavelengths, and the optical transmissivity should be at least 80%.

Examples of such materials include quartz glass, borosilicate glass, chemically reinforced glass, and other such sheet glass, and PET, drawn polypropylene, polyvinyl chloride, and other such organic macromolecular compounds. Borosilicate glass exhibits optical transmissivity of at

least 80% at wavelengths ranging from 330 nm to 2.6 μm, while quartz glass exhibits high optical transmissivity at even shorter wavelengths.

Furthermore, it is good to provide an anti-reflective layer of MgF2 or the like to the surface of the protective layer 4 because the stimulating light and stimulated emission will be transmitted more efficiently, and this will also lessen the decrease in sharpness.

When the protective layer 4 is provided directly over the stimulable phosphor layer 3, the material that makes up this protective layer can be cellulose acetate, nitrocellulose, polymethyl methacrylate, polyvinyl butyral, polyvinyl formal, polycarbonate, polyester, polyethylene terephthalate, polyethylene, vinylidene chloride, nylon, or the like. This protective layer 4 may be formed by building up an inorganic substance such as SiC, SiO2, SiN, or Al2O3 by metallizing, sputtering, or another such method. In this case, if the protective layer is provided directly to the phosphor layer, the thickness of the protective layer 4 should be 0.1 to 100 μm, and if the space 4A is provided, this thickness should be 50 μm to 5 mm, and preferably 100 μm to 3 mm.

The thickness of the protective layer 4 is 50 μm to 5 mm, but a range of 100 μm to 3 mm is preferable in order to obtain good moisture resistance.

With the radiation image conversion panel of the

present invention, a colored layer may be provided to the side closer to where the stimulating light is incident than the metal surface of the support 1 in order to further enhance the sharpness of the image.

This colored layer may be provided over the entire stimulable phosphor layer 3, or it may be provided just to the surface layer part of the stimulable phosphor layer 3, or to the layer portion closest to the metal surface of the support 1, or to the protective layer 4. Or, two or more layers may be provided. The transparent thin film layer in the present invention may also be colored.

This colored layer serves to absorb at least part of the stimulating light used to stimulate the stimulable phosphor to emission, and preferably has optical absorption characteristics such that the average reflectance with respect to light in the stimulating light wavelength band is less than the average reflectance with respect to light in the stimulated emission wavelength band.

An organic or inorganic colorant can be used for the colorant here, and in terms of hue, a blue or green colorant is preferable.

The "stimulable phosphor" referred to in the present invention is a phosphor that exhibits stimulated emission corresponding to the amount of irradiation with initial light or high-energy radiation when excited (stimulated) optically, thermally, mechanically, chemically, electrically, or

otherwise after being irradiated with initial light or high-energy radiation, but for practical purposes, a phosphor that exhibits stimulated emission [when irradiated] with stimulating light with a wavelength of at least 500 nm is preferable.

Any of the following can be used as the stimulable phosphor that makes up the stimulable phosphor layer.

(1) A phosphor expressed by $BaSO_4:A_x$ (where A is at least one of Dy, Tb, and Tm, and x is a number that satisfies $0.001 \leq x < 1$ mole %) as disclosed in Japanese Laid-Open Patent Application S48-80487

(2) A phosphor expressed by $SrSO_4:A_x$ (where A is at least one of Dy, Tb, and Tm, and x is a number that satisfies $0.001 \leq x < 1$ mole %) as disclosed in Japanese Laid-Open Patent Application S48-80489

(3) A phosphor obtained by adding at least one of Mn, Dy, and Tb to Na_2SO_4, $CaSO_4$, $BaSO_4$, or the like, as disclosed in Japanese Laid-Open Patent Application S51-29889

(4) A phosphor such as BeO, LiF, $MgSO_4$, or CaF_2 as disclosed in Japanese Laid-Open Patent Application S52-30487

(5) A phosphor such as $Li_2B_4O_7$:Cu,Ag as disclosed in Japanese Laid-Open Patent Application S53-39277

(6) A phosphor such as $Li_2O \cdot (B_2O_2)_x$:Cu (where x is a number that satisfies $2 < x \leq 3$) or $Li_2O \cdot (B_2O_2)_x$:Cu,Ag (where x is a number that satisfies $2 < x \leq 3$) as disclosed in Japanese Laid-Open Patent Application S54-47883

(7) A phosphor expressed by SrS:Ce,Sm, SrS:Eu,Sm, La2O2S:Eu,Sm, or (Zn, Cd)S:Mn,X (where X is a halogen) as disclosed in U.S. Patent 3,859,527

(8) A phosphor ZnS:Cu,Pb phosphor as disclosed in Japanese Laid-Open Patent Application S55-12142

(9) A barium alumate phosphor expressed by the general formula BaO · xAl2O3:Eu (where x is a number that satisfies $0.8 \leq x \leq 10$) as disclosed in Japanese Laid-Open Patent Application S55-12142

(10) An alkaline earth metallosilicate-based phosphor expressed by the general formula MAO · xSiO2:A (where MA is Mg, Ca, Sr, Zn, Cd, or Ba, A is at least one of Ce, Tb, Eu, Tm, Pb, Tl, Bi, and Mn, and x is a number that satisfies $0.5 \leq x < 2.5$) as disclosed in Japanese Laid-Open Patent Application S55-12142

(11) A phosphor expressed by the general formula (Ba1-x-yMgxCay)FX:eEu2+ (where X is at least one of Br and Cl, and x, y, and e are numbers that satisfy $0 < x + y \leq 0.6$, $xy \neq 0$, and $10-3 \leq e \leq 5 \times 10-2$, respectively) as disclosed in Japanese Laid-Open Patent Application S55-12142

(12) A phosphor expressed by the general formula LnOX:xA (where Ln is at least one of La, Y, Gd, and Lu, X is at least one of Cl and Br, A is at least one of Ce and Tb, and x is a number that satisfies $0 < x < 0.1$) as disclosed in Japanese Laid-Open Patent Application S55-12142

(13) A phosphor expressed by the general formula

$(Ba_{1-x}(MA)_x)FX:yA$ (where MA is at least one of Mg, Ca, Sr, Zn, and Cd, X is at least one of Cl, Br, and I, A is at least one of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, and Er, and x and y are numbers that satisfy $0 \leq x \leq 0.6$ and $0 \leq y \leq 0.2$, respectively) as disclosed in Japanese Laid-Open Patent Application S55-12145

(14) A phosphor expressed by the general formula $BaFX:xCe,yA$ (where X is at least one of Cl, Br, and I, A is at least one of In, Tl, Gd, Sm, and Zr, and x and y are numbers that satisfy $0 < x \leq 2 \times 10^{-1}$ and $0 < y \leq 5 \times 10^{-2}$, respectively) as disclosed in Japanese Laid-Open Patent Application S55-84389

(15) A rare earth element-activated divalent metallic fluorohalide phosphor expressed by the general formula $MAFX \cdot xA:yLn$ (where MA is at least one of Mg, Ca, Ba, Sr, Zn, and Cd, A is at least one of BeO, MgO, CaO, SrO, BaO, ZnO, Al_2O_3, Y_2O_3, La_2O_3, In_2O_3, SiO_2, TiO_2, ZrO_2, GeO_2, SnO_2, Nb_2O_5, Ta_2O_5, and ThO_2, Ln is at least one of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sm, and Gd, X is at least one of Cl, Br, and I, and x and y are numbers that satisfy $5 \times 10^{-5} \leq x \leq 0.5$ and $0 < y \leq 0.2$, respectively) as disclosed in Japanese Laid-Open Patent Application S55-160078

(16) A phosphor expressed by the general formula ZnS:A, (Zn,Cd)S:A, CdS:A, ZnS:A,X, or CdS:A,X (where A is Cu, Ag, Au, or Mn, and X is a halogen) as disclosed in Japanese Laid-Open Patent Application S55-160078

(17) A phosphor expressed by

General Formula I: $xM_3(PO_4)_2 \cdot NX_2:yA$ or

General Formula II: $M_3(PO_4)_2 \cdot yA$

(where M and N are each at least one of Mg, Ca, Sr, Ba, Zn, and Cd, X is at least one of F, Cl, Br, and I, A is at least one of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sb, Tl, Mn, and Sn, and x and y are numbers that satisfy $0 < x \leq 6$ and $0 \leq y \leq 1$, respectively) as disclosed in Japanese Laid-Open Patent Application S59-38278

(18) A phosphor expressed by

General Formula III: $nReX_3 \cdot mAX'_2:xEu$ or

General Formula IV: $nReX_3 \cdot mAX'_2:xEu,ySm$

(where Re is at least one of La, Gd, Y, and Lu, A is at least one alkaline earth metal from among Ba, Sr, and Ca, X and X' are at least one of F, Cl, and Br, x and y are numbers that satisfy $1 \times 10^{-4} < x < 3 \times 10^{-1}$ and $1 \times 10^{-4} < y < 1 \times 10^{-1}$, respectively, and n/m is a number that satisfies $1 \times 10^{-3} < n/m < 7 \times 10^{-1}$) as disclosed in Japanese Laid-Open Patent Application S59-155487

(19) A phosphor expressed by the general formula $aBaX_2 \cdot (1 - a)BaY_2:bEu^{2+}$ (where X and Y are each at least one of F, Cl, Br, and I, $X \neq Y$, and a and b are numbers that satisfy $0 < a < 1$ and $10^{-5} < b < 10^{-1}$, respectively) as disclosed in Japanese Laid-Open Patent Application H2-58593

(20) An alkali halide phosphor expressed by the general formula $M^AX \cdot aM^BX'_2 \cdot bM^CX''_3:cA$ (where M^A is at least one

alkali metal from among Li, Na, K, Rb, and Cs, MB is at least one divalent metal from among Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu, and Ni, MC is at least one trivalent metal from among Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga, and In, X, X', and X" are at least one halogen from among F, Cl, Br, and I, A is at least one metal from among Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, and Mg, and a, b, and c are numbers that satisfy $0 \leq a < 0.5$, $0 \leq b < 0.5$, and $0 < c \leq 0.2$, respectively) as disclosed in Japanese Laid-Open Patent Application S61-72087.

In the present invention, this alkali halide phosphor can be used to particular advantage because it is preferable for metallizing.

The present invention is not limited, however, to the phosphors listed above, and any other phosphor can also be used as long as it is one that exhibits stimulated emission when irradiated first with radioactive rays and then with stimulating light.

Fig. 3 is a simplified view of a radiation image conversion apparatus in which the radiation image conversion panel of the present invention is used. Reference numeral 5 is a radiation generator, 6 is a subject, 7 is a radiation image conversion panel, 8 is a stimulating light source, 9 is a photo-electric converter that detects stimulated

emission from the radiation image conversion panel 7, 10 is a reproduction unit for reproducing as images the signals detected by the photo-electric converter 9, 11 is a display unit for displaying the images reproduced by the reproduction unit 10, and 12 is a filter for separating the stimulating light and stimulated emission so that only the stimulated emission is transmitted.

With the radiation image conversion apparatus in Fig. 3, radiation R from the radiation generator 5 goes through the subject 6 and is incident on the radiation image conversion panel 7. This incident radiation RI is absorbed by the stimulable phosphor layer 3 of the radiation image conversion panel 7, the energy thereof is accumulated, and an accumulated image of the radiation-transmitted image is formed. This accumulated image is then excited by the stimulating light from the stimulating light source 8 and radiated as stimulated emission.

The intensity of the stimulated emission thus radiated is proportional to the amount of accumulated radiation energy, so this optical signal can be subjected to photo-electric conversion with the photo-electric converter 9 (such as a photomultiplier tube), reproduced as an image by the reproduction unit 10, and displayed by the display unit 11, allowing the radiation-transmitted image of the subject 6 to be viewed.

Examples

Examples of the present invention will now be described along with comparative examples, but the present invention is not limited to these aspects.

Example 1

A metal layer composed of a deposited film of aluminum with a thickness of 2000 Å was formed by metallizing on a support consisting of a crystallized glass sheet with a thickness of 1.0 mm, the product of which was a support having a metal surface.

A transparent thin film layer composed of a deposited film of SiO_2 (optical transmissivity at 350 to 800 nm (hereinafter referred to simply as "optical transmissivity"): at least 90%) with a thickness of 2000 Å was formed by metallizing over the metal surface of this support.

The optical transmissivity of the transparent thin film layer was measured over a range of 190 to 900 nm using a spectrophotometer (Hitachi model 557), using a transparent sheet of quartz glass (1.0 mm thick) as a reference sample, and using the product of forming just a transparent thin film layer in a specific thickness over a transparent sheet of quartz glass (1.0 mm thick) as the measurement sample. The same spectrophotometer was also used to measure the optical transmissivity of the protective layer.

The support on which the transparent thin film layer had been provided was placed in a metallizing apparatus, the temperature of the support was raised to 200°C and the degree of vacuum inside the metallizing apparatus was set to 10-6 Torr, and metallizing was performed under conditions such that the rate of deposition of metallizing substance onto the transparent thin film layer would be 5 μm/min, which formed a stimulable phosphor layer composed of a metallized film of a stimulable phosphor (RbBr:Tl) with a thickness of 300 μm over the transparent thin film layer.

Annealing was then performed at a temperature of 400°C in order to raise the crystallinity of the stimulable phosphor layer.

Following this annealing, a glass-sealed protective layer was provided over the stimulable phosphor layer with a space in between, which yielded the radiation image conversion panel A of the present invention shown in Fig. 1. The space was filled with dry nitrogen gas.

Example 2

A radiation image conversion panel B of the present invention was obtained in the same manner as in Example 1, except that the transparent thin film layer was changed to a transparent thin film layer composed of a metallizing film of MgF2 with a thickness of 2000 Å (optical transmissivity: at least 90%).

Example 3

A radiation image conversion panel C of the present invention was obtained in the same manner as in Example 1, except that the metal layer was changed to a metallizing film composed of chromium with a thickness of 2000 Å, and the thickness of the transparent thin film layer was changed to 3000 Å.

Example 4

A radiation image conversion panel D of the present invention was obtained in the same manner as in Example 1, except that the metal layer was changed to a metallizing film composed of chromium with a thickness of 2000 Å, and the transparent thin film layer was changed to one with a two-layer structure comprising a metallizing film of ZrO with a thickness of 1000 Å and a metallizing film of SiO2 with a thickness of 1000 Å.

Example 5

A radiation image conversion panel E of the present invention was obtained in the same manner as in Example 1, except that the transparent thin film layer was changed to a transparent thin film layer composed of a metallizing film of SiN with a thickness of 2000 Å (optical transmissivity: at least 80%).

Example 6

A radiation image conversion panel F of the present invention was obtained in the same manner as in Example 1, except that the support was changed to a support composed of an aluminum sheet with a thickness of 0.3 mm.

Example 7

A radiation image conversion panel G of the present invention was obtained in the same manner as in Example 6, except that the transparent thin film layer was changed to a transparent thin film layer composed of a metallizing film of MgF_2 with a thickness of 2000 Å (optical transmissivity: at least 90%).

Example 8

A radiation image conversion panel H of the present invention was obtained in the same manner as in Example 6, except that the transparent thin film layer was changed to a transparent thin film layer composed of a metallizing film of SiC with a thickness of 2000 Å (optical transmissivity: at least 90%).

Example 9

A coating solution for forming a stimulable phosphor layer was prepared by mixing and dispersing 8 weight parts of an RbBr:Tl stimulable phosphor with an average particle size of 8.5 μm and 1 weight part polyvinyl butyral resin in 8 weight parts solvent (cyclohexanone).

A sheet of crystallized glass with a thickness of 1.0 mm, on which a metal layer composed of a metallizing film of aluminum with a thickness of 2000 Å had been formed by metallizing, and on which a transparent thin film layer composed of a metallizing film of SiO_2 with a thickness of 2000 Å had also been formed by metallizing, was placed as a support on a horizontally leveled surface plate, and a frame was provided around the four sides of this support to prevent the above-mentioned coating solution from running out.

The coating solution was cast over the protective layer and left overnight at 25°C to allow the stimulable phosphor particles to settle out and form a stimulable phosphor layer. After this, the stimulable phosphor layer was further dried, and over this a glass-sealed protective layer was provided with a space in between, which yielded the radiation image conversion panel I of the present invention with the structure shown in Fig. 1.

The thickness of the stimulable phosphor layer in this radiation image conversion panel I was 300 μm.

Example 10

A coating solution for forming a stimulable phosphor layer was prepared by mixing and dispersing 8 weight parts of a BaFBr:Eu stimulable phosphor with an average particle size of 8.5 μm and 1 weight part polyvinyl butyral resin in 8 weight parts solvent (cyclohexanone).

A polyethylene film that had been separately formed in a thickness of 5 µm was placed as a protective layer on a horizontally leveled surface plate, and a frame was provided around the four sides of this protective layer to prevent the above-mentioned coating solution from running out.

The coating solution was cast over the protective layer and left overnight at 25°C to allow the stimulable phosphor particles to settle out and form a stimulable phosphor layer. After this, the stimulable phosphor layer was further dried, and over this was bonded as a support a polyethylene terephthalate film into which carbon black had been kneaded and which had a thickness of 200 µm, and on which a metal layer composed of a metallizing film of aluminum in a thickness of 2000 Å had been formed by metallizing, and on which a transparent thin film layer composed of a metallizing film of SiO2 with a thickness of 2000 Å had also been formed by metallizing. This yielded the radiation image conversion panel J of the present invention.

The thickness of the stimulable phosphor layer in this radiation image conversion panel J was 300 µm.

Comparative Examples 1 to 10

Comparative radiation image conversion panels a to j were obtained in the same manner as in Examples 1 to 10, respectively, except that no transparent thin film layer was

provided.

Evaluation

The radiation image conversion panels A to J pertaining to the present invention and the comparative radiation image conversion panels a to j obtained above were each used to produce a radiation image conversion apparatus with the structure shown in Fig. 3. A test was conducted in which actual images were formed, and the radiation sensitivity and image sharpness were evaluated.

Also, the radiation image conversion panels A to J and a to j were each subjected to an accelerated aging test by being left for 60 days at a temperature of 45°C and a relative humidity of 85%, and the radiation sensitivity and image sharpness after this test were examined in the same manner as above.

These results are compiled in Tables 1 and 2 below.

The radiation sensitivity and sharpness in Tables 1 and 2 are relative values when the values obtained in Examples 1 and 9 were used as a basis of 100. The radiation sensitivity is the amount of emission upon stimulation with semiconductor laser light following X-ray irradiation. The sharpness was evaluated by examining the modification transmission function (MTF). [This sharpness value] is based on the sum of the resolution (%) when the spatial frequency was 0.5, 1.0, and 2.0 cycles/mm.

Table 1

	Support	Metal layer	Transparent thin film layer (optical transmissivity)	Radiation sensitivity	Sharpness		Support	Metal layer	Transparent thin film layer (optical trans.)	Radiation sensitivity	Sharpness
Ex. 1	crystallized glass 1.0 mm	aluminum 2000 Å	SiO_2 (≥ 90%) 2000 Å	100 (100)	100 (100)	Comp. Ex. 1	same as Ex. 1	same as Ex. 1	—	80 (75)	100 (95)
Ex. 2	crystallized glass 1.0 mm	aluminum 2000 Å	MgF_2 (≥ 90%) 2000 Å	95 (95)	100 (100)	Comp. Ex. 2	same as Ex. 2	same as Ex. 2	—	80 (75)	100 (95)
Ex. 3	crystallized glass 1.0 mm	chromium 2000 Å	SiO_2 (≥ 90%) 3000 Å	80 (80)	95 (95)	Comp. Ex. 3	same as Ex. 3	same as Ex. 3	—	5 (3)	65 (60)
Ex. 4	crystallized glass 1.0 mm	chromium 2000 Å	ZrO/SiO_2 (≥ 70%) 1000 Å each	70 (70)	100 (100)	Comp. Ex. 4	same as Ex. 4	same as Ex. 4	—	5 (3)	65 (60)
Ex. 5	crystallized glass 1.0 mm	aluminum 2000 Å	SiN (≥ 80%) 2000 Å	90 (90)	100 (100)	Comp. Ex. 5	same as Ex. 5	same as Ex. 5	—	80 (75)	100 (95)
Ex. 6	aluminum 0.3 mm	integrated with	SiO_2 (≥ 90%) 2000 Å	100 (100)	100 (100)	Comp. Ex.	same as Ex. 6	same as Ex. 6	—	80 (75)	100 (95)

		support	2000 Å			6					
Ex. 7	aluminum 0.3 mm	integrated with support	MgF_2 (≥ 90%) 2000 Å	95 (95)	100 (100)	Comp. Ex. 7	same as Ex. 7	same as Ex. 7	—	80 (75)	100 (95)
Ex. 8	aluminum 0.3 mm	integrated with support	SiC (≥ 90%) 2000 Å	90 (90)	100 (100)	Comp. Ex. 8	same as Ex. 8	same as Ex. 8	—	80 (75)	100 (95)

Table 2

	Support	Metal layer	Transparent thin film layer (optical transmissivity)	Radiation sensitivity	Sharpness		Support	Metal layer	Transparent thin film layer (optical trans.)	Radiation sensitivity	Sharpness
Ex. 9	crystallized glass 1.0 mm	aluminum 2000 Å	SiO_2 (≥ 90%) 2000 Å	100 (5)	100 (60)	Comp. Ex. 9	same as Ex. 9	same as Ex. 9	—	90 (2)	100 (60)
Ex. 10	PET 0.2 mm	aluminum 2000 Å	SiO_2 (≥ 90%) 2000 Å	95 (5)	100 (60)	Comp. Ex. 10	same as Ex. 10	same as Ex. 10	—	90 (2)	100 (60)

As is clear from Tables 1 and 2, good radiation sensitivity and sharpness are obtained with the radiation image conversion panels A to J of the present invention.

The reason such good results were obtained is believed to be that with the radiation image conversion panel of the present invention, the transparent thin film layer is present between the stimulable phosphor layer and the metal surface of the support, preventing contact between the two, and therefore the stimulable phosphor layer and the metal surface of the support remain in an extremely chemically stable state even during metallizing (at a temperature of 200°C) and annealing (at a temperature of 400°C).

The comparative radiation image conversion panels a to j, however, were inferior to the radiation image conversion panels A to J of the present invention in their radiation sensitivity and/or sharpness. This is believed to be because no transparent thin film layer was provided with the comparative radiation image conversion panels, so the metal surface of the support underwent a chemical reaction with the stimulable phosphor in the stimulable phosphor layer during annealing and became corroded, which resulted in inferior radiation sensitivity and image sharpness.

Effect of the Invention

As described in detail above, with the radiation image conversion panel of the present invention, a transparent thin

film layer is provided between the stimulable phosphor layer and the metal surface of the support, so there is no danger of the metal surface of the support being corroded by the stimulable phosphor in the stimulable phosphor layer and remains mechanically and chemically stable over an extended period, so the radiation sensitivity and image sharpness are good from the outset, and furthermore these good characteristics remain stable for an extended period.

4. Brief Description of the Drawings

Fig. 1 is a cross section of an example of the radiation image conversion panel of the present invention;

Fig. 2 is a cross section of another example of the radiation image conversion panel of the present invention; and

Fig. 3 is a simplified diagram of a radiation image conversion apparatus.

Key:

1 support

1A non-metal substrate

1B metal layer

1' metal support

2 transparent thin film layer

3 stimulable phosphor layer

4 protective layer

5 radiation image conversion apparatus

6 subject

7 radiation image conversion panel

8 stimulating light source

9 photo-electric converter

10 reproduction unit

11 display unit

12 filter

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Figure 1

Figure 2

Figure 3